

# Flow-Through and Batch Methods for Determining Calcium-Magnesium and Magnesium-Calcium Selectivity

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## ABSTRACT

Conducting binary-exchange experiments is a common way to identify cationic preferences of exchanger phases and the two most common approaches are the flow-through and batch methods. The objectives of this research were to provide the materials and methods for both flow-through and batch equilibration techniques and to compare Ca-Mg and Mg-Ca selectivity when using these two methods on a montmorillonitic soil. The methods were evaluated by comparing both the Gibbs free energy values ( $\Delta G_{\text{ex}}$ ) and selectivity diagrams derived from the flow-through and batch exchange reactions. The  $\Delta G_{\text{ex}}$  values for the Ca-Mg reaction were 634 and 444 J mol<sup>-1</sup> as determined by the flow-through and batch methods, respectively, indicating an exchanger preference for Ca. Exchanger preference for Ca was also evident in the Mg-Ca reaction with  $\Delta G_{\text{ex}}$  values of -882 and -784 J mol<sup>-1</sup> for the flow-through and batch methods, respectively. The flow-through and batch methods worked very well for determining cation selectivity and results indicate no significant differences existed between the two methods.

CATIONIC, BINARY-EXCHANGE EXPERIMENTS are a simple way to thermodynamically determine whether an exchanger phase selectively sorbs one cation in preference to another. Exchanger-phase equilibrium is commonly achieved by using either batch (Amrhein and Suarez, 1990; Bond, 1995; Curtin et al., 1998; El Prince et al., 1980; Endo et al., 2002; Evangelou and Lumbanraja, 2002; Feigenbaum et al., 1991; Fletcher et al., 1984; Karmarkar et al., 1991; Levy et al., 1972; Suarez and Zahow, 1989; Sposito et al., 1981, 1983b; Zhang and Sparks, 1996) or flow-through (Carlson and Buchanan, 1973; Chung and Zasoski, 1994; Jardine and Sparks, 1984; Jensen and Babcock, 1973; Naylor and Overstreet, 1969; Ogwada and Sparks, 1986; Shainberg et al., 1987; Thabet and Selim, 1996) systems. Batch systems typically require repeated washings of exchanger phases with characterized solutions until equilibrium between exchanger and solution phases exists. A flow-through system provides a continuous interaction between a solution phase of constant composition and the exchanger phase until equilibrium has been reached. The flow-through method also prevents unwanted loss of exchanger phase that may occur during decantation steps in a batch reaction.

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The flow-through and batch methods have been reported to produce comparable results when used for binary-exchange reactions (Feigenbaum et al., 1991; Grolimund et al., 1995; Thabet and Selim, 1996) but direct comparisons between these two methods are minimal (Grolimund et al., 1995). Thus, the objectives of this research are to: (i) provide a detailed outline of the supplies and procedures needed to perform binary-exchange reactions using the flow-through and batch equilibration techniques (ii) determine and compare Ca-Mg and Mg-Ca selectivity using both flow-through and batch methods.

## MATERIALS AND METHODS

Surface soil (0–30 cm), which was previously described in DeSutter and Pierzynski (2005) as S1, was used for all selectivity experiments. The soil is a fine, montmorillonitic, thermic, Vertic Argiustoll, containing 139, 506, and 354 g kg<sup>-1</sup> of sand, silt, and clay, respectively. The soil had a pH of 7.3, organic carbon content of 7.8 g kg<sup>-1</sup>, and cation exchange capacity (CEC) of 17.9 cmol<sub>c</sub> kg<sup>-1</sup>. The clay fraction was composed of mica-smectite-kaolinite assemblages and had a specific surface area of 334 m<sup>2</sup> g<sup>-1</sup>. The soil was Ca<sup>2+</sup> or Mg<sup>2+</sup> saturated using concentrated CaCl<sub>2</sub> or MgCl<sub>2</sub> solutions, respectively, rinsed with deionized water (DI) to remove excess salts, and allowed to dry at 25°C. After drying, the soil was finely ground to pass through a 1.0-mm sieve.

Solution phases were prepared by using 11 predetermined equivalent fractions of Ca and Mg. Equivalent fractions ranged from 0:1 (Ca/Mg) to 1:0 (Ca/Mg), while maintaining a constant ionic strength of 0.05 mol L<sup>-1</sup>. The 11 target solution concentrations were prepared by pipetting appropriate amounts of 2 M CaCl<sub>2</sub> and 2 M MgCl<sub>2</sub> solutions into tared 4-L bottles. The bottles were then filled to 4 kg by adding DI water, and the solutions were mixed. Concentrations of Ca and Mg in each solution were verified using inductively coupled plasma-atomic emission spectroscopy (ICP). From each 4-L bottle, 500 mL of solution was removed for use in the batch equilibrations and the remaining solutions in the 4-L bottles were used for the flow-through equilibrations.

## Flow-Through Method

A schematic diagram of the flow-through method is outlined in Fig. 1. The 4-L bottles were set up as Mariotte bottles to maintain a constant head of solution phase overlying the exchanger phase. The 4-L bottles were each fitted with a #6 two-hole stopper equipped with 6.4-mm OD vent- and solution-supply tubing with lengths of 80 and 120 cm, respectively. The solution-supply tube was routed to the inside of a 47-mm Teflon filter apparatus (1-47, 47-6, and 47, Saville Corp., Minnetonka, MN) that contained a 47-mm 0.45-μm filter (097191B, Fisher Scientific, Pittsburgh, PA). The outlet of

**Abbreviations:** DI, deionized water; CEC, cation exchange capacity; ICP, using inductively coupled plasma-atomic emission spectroscopy; RCF, relative centrifugal force.

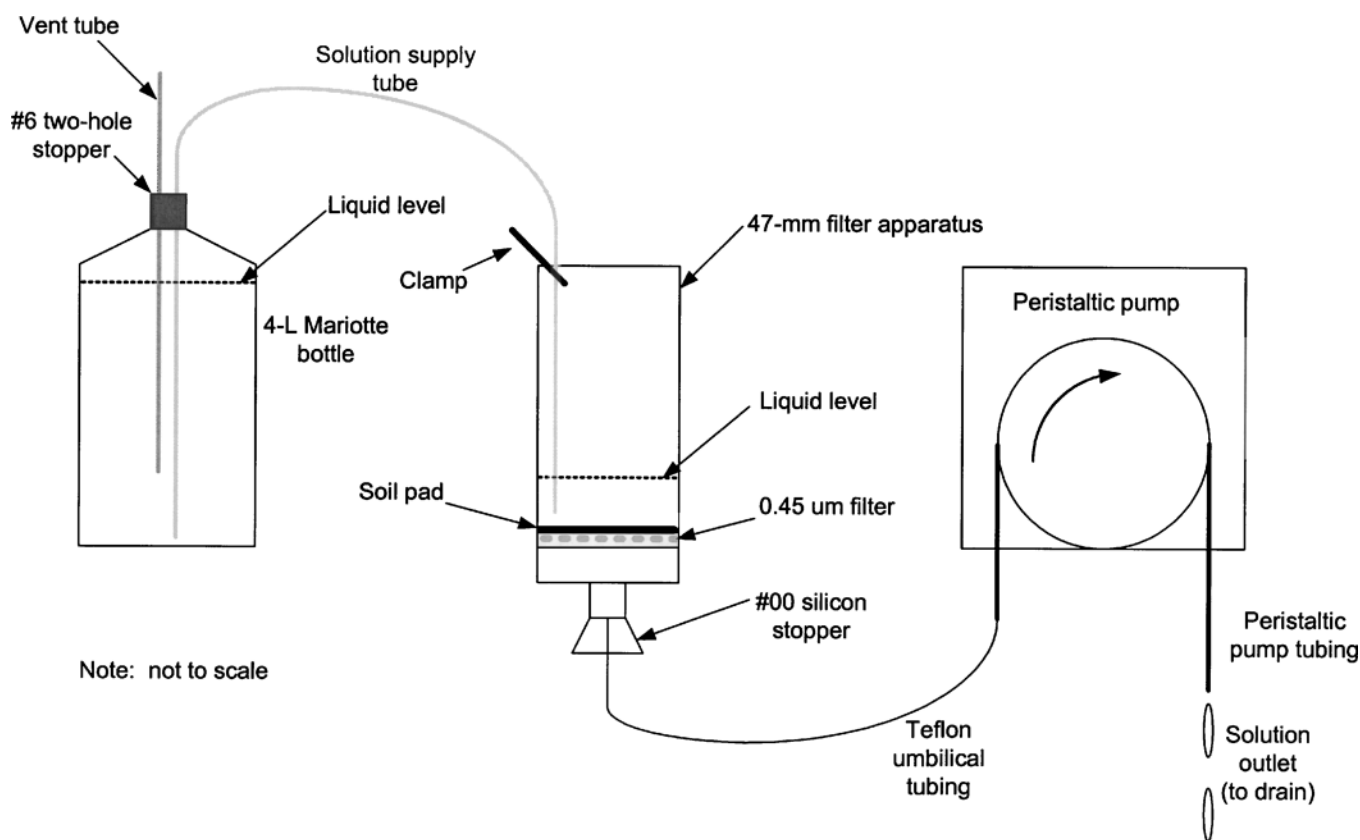


Fig. 1. Schematic drawing of the supplies and application design used to conduct the flow-through experiment.

the Teflon filter apparatus was plugged with a #00 silicon stopper (097041D, Fisher Scientific) fitted with a 1.6-mm OD Teflon umbilical tube (06406-60, Cole-Parmer Instr. Co., Vernon Hills, IL). The silicon stopper was previously center-drilled with a 1.6-mm drill bit, thus allowing the 1.6-mm OD umbilical tubing to be inserted until about 3 mm was protruding from the tapered end. The umbilical tubing was connected to 1.14-mm ID peristaltic-pump tubing (14190109, Fisher Scientific) that was fit into a 12-channel console-driven peristaltic pump (7520-10, Barnant Co., Barrington, IL).

One gram of soil was weighed into each of eleven 50-mL polypropylene tubes and suspended in 25 mL of DI water. The suspensions were transferred to the Teflon filter assemblies, and the water was removed using the peristaltic pump. Each solution phase was transferred to the filter assemblies by applying a positive pressure through the vent tube. The Mariotte bottle was positioned so that about a 5-cm layer of solution phase was maintained over the soil pad throughout the equilibration. Flow of solution phase was maintained at  $1.6 \text{ mL min}^{-1}$ , which provides 36 h for equilibration if all the 3.5 L of solution is used. Equilibration was achieved when the incoming and outgoing concentrations of Ca and Mg were equal. Preliminary experiments indicate that equilibration between solution and an exchanger phase occurs before all 3.5 L of solution has been used. Still, these preliminary experiments suggest that using all 3.5 L of solution ensures that equilibration has been achieved without the need to further analyze the solution phases during the course of the experiment. All equilibrations were performed at  $25^\circ\text{C}$  and a pressure of near 97.6 kPa. After equilibrations with the solution phases were complete, the soils were rinsed with 100 mL of 95% (v/v) ethanol to remove excess salts and allowed to dry at  $25^\circ\text{C}$ . Soils were removed from the filters and lightly ground using a glass-

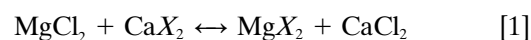
stirring rod. Calcium and Mg in each soil was extracted from 0.5 g of soil using 10 mL of 0.5 M Na-acetate by shaking on a horizontal shaker for 20 min and centrifuging for 20 min at a relative centrifugal force (RCF) of  $1136 \times g$  and Ca and Mg were determined using ICP.

### Batch Method

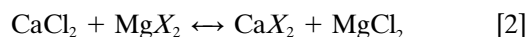
Batch reaction was achieved by adding 20 mL of equilibrating solution to 1.0 g of Ca or Mg-saturated soil that had been weighed into 50-mL polypropylene-centrifuge tubes. The soil/solution mixture was shaken for 20 min on a horizontal shaker, centrifuged for 20 min at a RCF of  $1136 \times g$ , and supernatant decanted and discarded. This process was repeated three times and in the last supernatant, concentrations of Ca and Mg were determined to ensure that the soil and solution phase were at equilibrium. After equilibrations, the soil was washed five times with 20 mL of 95% ethanol by shaking for 10 min on a horizontal shaker followed by centrifugation at a RCF of  $1136 \times g$ . After the washings were complete the soil was allowed to dry overnight at  $25^\circ\text{C}$  to remove excess ethanol. Calcium and Mg in each soil was extracted with 10 mL of 0.5 M sodium acetate by shaking on a horizontal shaker for 20 min and centrifuging for 20 min at a RCF of  $1136 \times g$ . The supernatant was removed through pipetting and saved. This process was repeated twice and the two 20-mL extractants were combined and Ca and Mg were determined using ICP.

### Analysis

For Ca-Mg exchange, the general binary-exchange reaction is



and for Mg-Ca exchange, the binary reaction is



where  $X$  represents 1  $M$  of surface negative charge on the exchanger phase. For each equilibration, the Vanselow selectivity coefficient ( $K_v$ ) was computed, from Bond and Verburg (1997), as

$$K_v^{ij} = \frac{x_j(\gamma_i C_i)}{x_i(\gamma_j C_j)} \quad [3]$$

where  $x$  is the mole fraction of Ca or Mg on the exchanger phase,  $\gamma$  is the solution activity coefficient of Ca or Mg, and  $C$  is the concentration of Ca or Mg in the solution phase ( $\text{mol L}^{-1}$ ). Solution concentrations were used to calculate ionic strengths of the solution phase. The extended Debye-Huckel equation was used to calculate the single-ion activity coefficients used to estimate activities of cations in the solution phase (Strumm and Morgan, 1996). Gibbs free energies ( $\Delta G_{\text{ex}}$ ) were calculated for each binary-exchange reaction from

$$\ln K_{\text{ex}} = \int_0^1 \ln K_v dE_i \quad [4]$$

and

$$\Delta G_{\text{ex}} = -RT \ln K_{\text{ex}} \quad [5]$$

where  $K_{\text{ex}}$  is the equilibrium exchange constant;  $E_i$  is the equivalent fraction of cation  $i$  on the exchanger;  $R$  is equal to  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ; and  $T$  is the reaction temperature, which was held constant at  $298 \text{ K}$  (Sparks, 2003). Each reported  $\Delta G_{\text{ex}}$  is the average of four replications. Furthermore, selectivity diagrams were constructed by plotting the equivalent fraction of cation  $i$  on the exchanger phase versus the equivalent fraction of cation  $i$  in the solution phase (Sparks, 2003). Nonpreference isotherms for these homovalent exchanges were 1:1 lines.

Descriptive statistics were determined for each equilibration method-exchange reaction combination and a Student's  $t$  test was used to compare equilibration methods within each exchange reaction.

## RESULTS AND DISCUSSION

The average CEC values for each exchanger test for the Ca-Mg exchange reactions were not statistically

influenced ( $p = 0.05$ ) by the flow-through and batch equilibration extraction procedures (Table 1). However, statistical differences between CEC values were observed for exchanger tests two and three for the Mg-Ca exchange reaction indicating that the sequential extraction used for the batch method yielded greater CEC values than the single extraction used for the flow-through method (Table 2). The average CEC values for the Ca-Mg exchange reactions for the flow-through and batch methods were  $16.5$  and  $16.9 \text{ cmol}_c \text{ kg}^{-1}$ , respectively (Table 1), and for the Mg-Ca exchange reactions were  $16.4$  and  $18.0 \text{ cmol}_c \text{ kg}^{-1}$ , respectively (Table 2).

The flow-through and batch techniques worked very well for equilibrating an exchanger phase with a solution phase. No Ca or Mg was detected in soil after treatment from the 100% Mg or 100% Ca solution, respectively, indicating complete ion exchange. The values of  $K_v$  for the flow-through and batch Ca-Mg equilibrations (Eq. [1]) were generally less than one indicating that Ca was preferred on the exchanger phase over Mg (Table 1). No significant differences ( $p = 0.05$ ) were observed between values of  $K_v$  for each exchanger test for the flow-through and batch equilibration methods (Table 1). These  $K_v$  values are similar to those reported by Jensen and Babcock (1972) in which their average  $K_v$  values for solutions with ionic strengths of  $0.01$  and  $0.001 \text{ mol L}^{-1}$  ranged from  $0.60$  to  $0.63$ . Exchange isotherms also indicate that Ca was preferred over Mg on the exchanger using both the flow-through and batch equilibration techniques (Fig. 1). The magnitude of Ca preference is described by the  $\Delta G_{\text{ex}}$  (Eq. [5]) that was  $634$  and  $444 \text{ J mol}^{-1}$  for the flow-through and batch equilibration techniques, respectively (Fig. 1). A Student's  $t$  test indicated that no significant difference was observed between the  $\Delta G_{\text{ex}}$  values from the two-equilibration techniques.

All  $K_v$  values for the Mg-Ca exchanges (Eq. [2]) for both equilibration techniques were greater than one, indicating that Ca was preferred on the exchanger over Mg (Table 2). No statistical differences ( $p = 0.05$ ) were observed between  $K_v$  values derived using the flow-

**Table 1. Binary exchange (Ca-Mg) solution and exchanger compositions, cation exchange capacity of the soil (CEC), and Vanselow selectivity coefficients ( $K_v$ ) for a montmorillonitic soil using flow-through and batch equilibration methods. Each number represents the average of four replications.**

Exchanger test	Flow-through method						Batch method			
	Solution composition		Exchanger composition		CEC	$K_v$	Exchanger composition		CEC	$K_v$
	Ca	Mg	Ca	Mg			Ca	Mg		
	—mol L <sup>-1</sup> —		—mol kg <sup>-1</sup> —		cmol <sub>c</sub> kg <sup>-1</sup>		—mol kg <sup>-1</sup> —		cmol <sub>c</sub> kg <sup>-1</sup>	
1	0.017	0.000	0.084	0.000	16.7(1.1)†		0.086	0.000	17.3(0.6)	
2	0.016	0.002	0.076	0.008	16.8(1.4)	0.99(0.18)	0.079	0.008	17.4(0.6)	1.01(0.11)
3	0.014	0.003	0.069	0.013	16.5(1.3)	0.76(0.17)	0.070	0.015	17.0(0.7)	0.90(0.04)
4	0.013	0.005	0.063	0.022	16.9(1.5)	0.84(0.08)	0.063	0.022	16.9(0.4)	0.85(0.03)
5	0.011	0.007	0.054	0.029	16.6(1.5)	0.81(0.06)	0.055	0.031	17.1(0.7)	0.89(0.10)
6	0.009	0.008	0.047	0.036	16.5(0.9)	0.80(0.03)	0.048	0.036	16.8(0.5)	0.81(0.06)
7	0.007	0.010	0.039	0.045	16.8(1.4)	0.79(0.02)	0.040	0.045	16.9(0.6)	0.80(0.07)
8	0.006	0.012	0.031	0.052	16.7(1.1)	0.75(0.01‡)	0.032	0.053	16.9(0.7)	0.79(0.07)
9	0.004	0.013	0.022	0.061	16.7(1.2)	0.73(0.01‡)	0.023	0.061	16.9(0.6)	0.77(0.09)
10	0.002	0.015	0.012	0.070	16.4(1.4)	0.67(0.02)	0.013	0.070	16.8(0.5)	0.79(0.14)
11	0.000	0.017	0.000	0.077	15.3(0.8)		0.000	0.079	15.8(0.9)	

† Values in parentheses represent the standard deviations.

‡ Value  $\leq 0.01$ .

**Table 2.** Binary exchange (Mg-Ca) solution and exchanger compositions, cation exchange capacity of the soil (CEC), and Vanselow selectivity coefficients ( $K_v$ ) for a montmorillonitic soil using flow-through and batch equilibration methods. Each number represents the average of four replications.

Exchanger test	Solution composition		Flow-through method				Batch method			
	Exchanger composition		Exchanger composition		CEC	$K_v$	Exchanger composition		CEC	$K_v$
	Ca	Mg	Mg	Ca			Mg	Ca		
	—mol L <sup>-1</sup> —		—mol kg <sup>-1</sup> —		cmol <sub>c</sub> kg <sup>-1</sup>		—mol kg <sup>-1</sup> —		cmol <sub>c</sub> kg <sup>-1</sup>	
1	0.000	0.017	0.075	0.000	14.9(0.4)†		0.087	0.000	17.3(2.1)	
2	0.002	0.015	0.067	0.013	16.1‡(1.0)	1.71(0.35)	0.078	0.013	18.2‡(1.1)	1.54(0.08)
3	0.003	0.013	0.057	0.023	16.0§(1.2)	1.51(0.15)	0.068	0.024	18.3§(0.8)	1.44(0.07)
4	0.005	0.011	0.050	0.032	16.4(1.4)	1.44(0.13)	0.058	0.033	18.2(1.0)	1.38(0.08)
5	0.007	0.010	0.043	0.040	16.5(1.2)	1.38(0.07)	0.047	0.043	18.0(1.0)	1.32(0.09)
6	0.009	0.008	0.034	0.048	16.4(1.7)	1.34(0.05)	0.041	0.050	18.1(1.1)	1.30(0.09)
7	0.010	0.007	0.027	0.056	16.6(1.6)	1.32(0.02)	0.031	0.057	17.7(1.5)	1.31(0.11)
8	0.012	0.005	0.020	0.063	16.6(1.3)	1.28(0.03)	0.024	0.067	18.2(1.0)	1.28(0.12)
9	0.014	0.003	0.013	0.070	16.9(1.4)	1.28(0.02)	0.016	0.074	18.0(1.2)	1.29(0.16)
10	0.016	0.002	0.007	0.077	16.8(1.2)	1.17(0.11)	0.009	0.083	18.3(1.1)	1.28(0.22)
11	0.017	0.000	0.000	0.086	17.1(1.0)		0.000	0.090	17.9(1.2)	

† Values in parentheses represent the standard deviation.

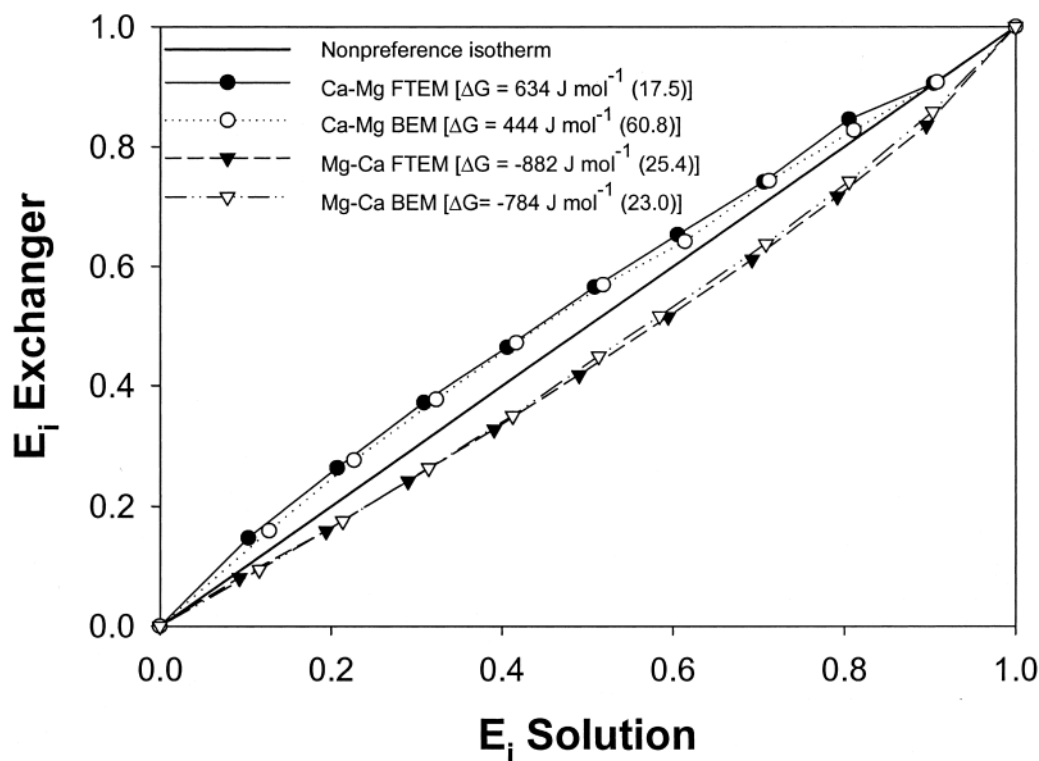
‡ Values are significantly different at the  $p = 0.05$  level.

§ Values are significantly different at the  $p = 0.05$  level.

through and batch methods for all exchanger tests (Table 2). Exchange isotherms also indicate that the exchanger phase preferentially adsorbed Ca over Mg (Fig. 2). The  $\Delta G_{ex}$  values for (Eq. [2]) for the flow-through and batch techniques were  $-882$  and  $-784$  J mol<sup>-1</sup>, respectively, and a Student's  $t$  test indicated that no significant difference was observed between the two methods.

Soil preference for Ca over Mg has been commonly reported in the literature (Beckett, 1965; Fletcher et al.,

1984; Jensen and Babcock, 1973; Sposito and Fletcher, 1985; Suarez and Zahow, 1989; Thabet and Selim, 1996; Van Bladel and Gheyi, 1980). In pure montmorillonitic clays, Ca and Mg have equal affinities for exchange sites (Sposito et al., 1983a). However, when organic C is present in the exchanger system the preference shift is toward Ca (Baes and Bloom, 1988; Curtin et al., 1998; Fletcher et al., 1984; Van Bladel and Gheyi, 1980). Also, a Student's  $t$  test did not indicate that hysteresis was present in either the flow-through or batch methods and



**Fig. 2.** Calcium-Mg and Mg-Ca exchange isotherms and average values for the Gibbs free energy of exchange ( $\Delta G_{ex}$ ) for a montmorillonitic soil derived using flow-through (FTEM) and batch (BEM) equilibration methods. Numbers in parentheses following the  $\Delta G_{ex}$  values are the coefficients of variation of the  $\Delta G_{ex}$  replications.  $E_i$  represents the equivalent fraction of Ca or Mg in the solution and exchanger phase for either the Ca-Mg or Mg-Ca reaction, respectively.



thus the reactions are considered thermodynamically reversible (Verburg and Baveye, 1994).

An advantage of the flow-through method is that the soil sample is not handled during the equilibration step with the solution phase whereas in the batch method the supernatant is repeatedly decanted from reaction tubes which may carry with it soil particles. Although Thabet and Selim (1996) report that batch techniques can take 3 to 5 d to complete, the batch method outlined here required about 9 h to complete a set of equilibrations (11 equilibrating solutions) as outlined in Tables 1 and 2. For the flow-through method, the total time requirement for a complete set of equilibrations was about 35 h with 32 of those hours being the equilibration and ethanol washing stages, which are unattended.

## CONCLUSIONS

The flow-through and batch techniques have both shown to be equally effective methods for determining the preference of Ca over Mg on the soil exchange sites. There were no statistical differences between the two methods. A detailed outline of the equipment and procedures needed to conduct flow-through equilibrations is provided. The advantages of the flow-through method over the batch method include a one-time characterization of the solution phase during the experiment, no potential losses of sample during the solution-exchanger equilibration reaction, and reduced labor requirement. Potential disadvantages of the flow-through method may include initial equipment costs, the cost associated with preparing equilibrating solutions, and the overall length of time from the onset to the conclusion of the experiment. However, the time required for the equilibration step using the flow-through method may be reduced depending on the quantity of the exchanger and goals of the experiment.

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